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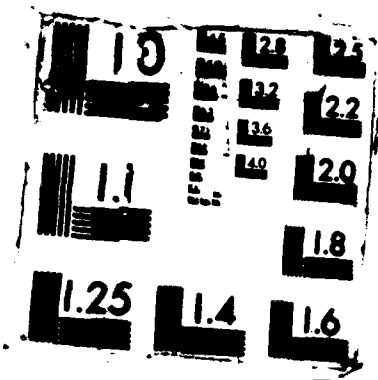
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**STATISTICAL FINE STRUCTURE OF
INHOMOGENEOUSLY BROADENED ABSORPTION LINES**

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ABSTRACT: Using laser frequency-modulation spectroscopy, we have observed statistical fine structure (SFS) in the inhomogeneously broadened optical absorption of pentacene in p-terphenyl at liquid helium temperatures. SFS is the actual frequency-dependent, time-independent structure of the inhomogeneous line caused by the randomly varying number of centers in each frequency interval. The size of the SFS varies as the square root of the number of centers, and the autocorrelation of the SFS yields an estimate of the homogeneous linewidth without requiring spectral hole-burning or coherent transients.

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Inhomogeneous broadening¹ is a common feature of the low-temperature spectra of impurity centers in solids² that can appear in nuclear magnetic resonance, electron spin resonance, optical absorption³, and Mössbauer absorption. For zero-phonon transitions in crystals, the inhomogeneous profile (for a particular orientation or site) is composed of many narrow homogeneous absorption lines with a distribution of center frequencies caused by dislocations, point defects, or random internal electric fields and field gradients. In an amorphous host, it is principally the large multiplicity of available sites that leads to inhomogeneous broadening.

Inhomogeneously broadened absorption lines are generally regarded as being smooth. In this paper we point out the surprising fact that significant fine structure is a fundamental property of such lines. Consider a fixed frequency interval $\Delta\nu$ within the inhomogeneous line that satisfies $\Delta\nu_I > \Delta\nu > \Delta\nu_H$, where $\Delta\nu_H$ is the full homogeneous linewidth at half-maximum absorption (FWHM) and $\Delta\nu_I$ is the FWHM of the inhomogeneous line. When the various centers are independent and isolated, statistical physics⁴ requires that as the number N of centers in the probed volume with center frequencies in $\Delta\nu$ increases, the average absorption coefficient over the interval increases linearly with N while the rms statistical variations in the absorption coefficient grow only as $N^{1/2}$. These variations in the absorption coefficient are caused by the different number of centers in each frequency interval. We use the phrase "statistical fine structure" (SFS) to refer to the static, time-independent, frequency-dependent variations in inhomogeneously broadened absorption lines. Since the relative size of the SFS scales as $N^{-1/2}$, small N samples ($N < 100$, for example) would be expected to be optimal for the observation of SFS; however, detecting a small number of centers in the presence of considerable background signals from the host matrix is quite difficult⁵.

We have observed for the first time statistical fine structure in the inhomogeneously broadened optical absorption of pentacene molecules in p-terphenyl crystals and polycrystals at liquid helium temperatures. This has been accomplished in a high N sample by the realization that a zero-background technique, laser frequency-modulation (FM) spectroscopy⁶, is more sensitive to SFS in this limit than when N is small, as long as sufficient light reaches the detector. This is because FM spectroscopy measures only the difference in optical absorption at two sidebands displaced symmetrically about the carrier by the modulation frequency, and not the background absorption. Hence the FM signal due to SFS grows approximately as $N^{1/2}$ and therefore is easier to detect when N is large. We demonstrate that information about the statistics of the centers and about $\Delta\nu_H$ can be derived from the SFS spectra, without requiring spectral hole-burning or coherent transients.

Samples for this study were prepared from mixtures of sublimed pentacene and zone-refined p-terphenyl which were either (i) heated between glass cover slips at ≈ 220 C and then cooled to form a 10 - 20 μm thick polycrystalline thin film with ≈ 50 μm x 50 μm crystalline regions, or (ii) grown into single crystals using Bridgman techniques. Concentrations ranged between 4×10^{-4} and 2×10^{-6} mole/mole, yielding low temperature optical densities at the peak of the O_1 site absorption^{7, 8} between 0.02 and 0.2.

Standard FM techniques⁹ employing an AD P electro-optic phase modulator and a Si avalanche photodiode were used to phase-sensitively detect the SFS signal. Complete details of the apparatus will be presented elsewhere¹⁰. The crucial feature of the FM technique is that the detected signal in the quadrature phase, $F(\nu)$, is proportional to

$$F(\nu) \sim -MP_0 e^{-2\delta_0} [\delta(\nu + \nu_m) - \delta(\nu - \nu_m)], \quad (1)$$

where ν is the laser frequency, ν_m is the rf modulation frequency, P_0 is the laser power on the sample, M is the modulation index, $\delta(\nu) = \alpha(\nu)L/2$, with α the absorption coefficient and L the sample length, and δ_0 is the background value of δ . Thus as long as δ_0 is not large, the FM signal measures the difference in αL at the two sideband frequencies.

A simple approximation helps in understanding the influence of various material parameters on the size of the SFS signals. Let ΔN and $\Delta\alpha$ signify the rms amplitudes of the variations of N and α over $\Delta\nu$, then $(\Delta\alpha)L = \alpha_0 L(\Delta N/N_0) = \alpha_0 L(N_0)^{-1/2} = \sigma(n_v L/A)^{1/2}$, where α_0 and N_0 signify the mean values of these quantities over $\Delta\nu$, σ is the peak absorption cross section, A is the beam area, and the volume density $n_v = N_0/AL$. Now when ν_m is larger than the width of the spectral features, the FM signal measures the size of $\Delta\alpha L$ directly. Therefore, the FM signal increases if the concentration of absorbers or the sample length is increased, but decreases with increasing laser spot size. Further, centers with higher cross section lead to larger FM signals due to SFS.

Figure 1 shows FM spectra of SFS under varying conditions for pentacene in a single crystal of p-terphenyl. These spectra were acquired by scanning a R6G single-frequency dye laser repetitively over the desired frequency range and averaging 64 scans. Unless stated otherwise, the laser was focused to a 20 μm diameter spot, and the sample was immersed in superfluid helium at 1.4 K. Trace 1(a) shows the amplifier noise floor. In 1(b), the laser was set 50 cm^{-1} away from the 2 cm^{-1} FWHM O_1 site absorption to show the laser noise (shot + avalanche). In 1(c), the laser wavelength was set near the peak of the O_1 line. The striking frequency-dependent structure is due to SFS, i.e., the superposition of a large number of individual homogeneous lineshapes with a distribution of center frequencies. We emphasize that at a fixed spot in the sample and for a fixed spectral range, the SFS signals are static and repeatable, as evidenced by 1(d) (overlaid with 1(c)) acquired under identical conditions. In

1(e), the focused laser spot has been moved to another location in the crystal; the SFS has changed reflecting the different statistical sample. In 1(f), the center frequency of the laser scan has been shifted by 50 MHz from that for 1(e).

Trace 1(g) shows that the amplitude of the SFS indeed drops for a larger laser spot. Trace 1(h) (overlaid with 1(g)) shows another interesting effect: a persistent spectral hole can be formed if the unmodulated laser beam is held fixed at the frequency corresponding to the center of the trace for 30 s with the power increased to 11 mW. Because of this low-efficiency hole-burning, the total laser intensity at the sample during probing was kept below 2 W/cm^2 to minimize the formation of hole trenches¹¹ that could alter the structure of the SFS. The hole in 1(h) is power-broadened (43 MHz FWHM); using an unfocused (3 mm diameter) laser beam and 2 μW burn power, the hole width at the detection limit was measured to be 19.6 MHz FWHM. This is the first reported observation of persistent spectral hole formation for the pentacene/p-terphenyl system. Since the guest is photostable and the host is crystalline, the hole formation process may involve reorientation of the pentacene in the host as has been observed in other crystals containing photostable guests¹². In any case, the hole-burning effect is an important topic for future studies.

The finest structure on the SFS signal is related to $\Delta\nu_H$. We recall that FM spectra have two well-defined limits depending upon the ratio of ν_m to the linewidth of the spectral features under consideration⁹. For a single Lorentzian profile with width $\Delta\nu_H$, when $\nu_m > \Delta\nu_H$ the FM lineshape consists of two replicas of the Lorentzian line, one positive and one negative, separated by $2\nu_m$. In this regime the amplitude of the FM signal is maximal and independent of ν_m . However, if $\nu_m < \Delta\nu_H$, the FM signal approaches the derivative of the Lorentzian lineshape, and the amplitude of the FM signal approaches zero with decreasing ν_m . For

pentacene in p-terphenyl at 1.4 K, $\Delta\nu_H$ has been reported to be 6.5-7.8 MHz^{13,14}. Thus for traces 1(c) - 1(h), the $\nu_m > \Delta\nu_H$ limit applies.

Since the homogeneous linewidth of pentacene in p-terphenyl grows exponentially with temperature¹³, the small ν_m limit can be achieved by raising the temperature of the sample. One would expect the SFS signal to disappear when $\Delta\nu_H$ becomes much larger than ν_m . This is illustrated by traces 1(i), 1(j), and 1(k) which are in-focus scans taken at 1.4 K, 5.6 K, and 7 K, respectively, corresponding to homogeneous linewidths of 6.5 MHz, 68 MHz, and 250 MHz.

Results similar to those in Fig. 1 were obtained for the O₂ site, but the O₃ and O₄ sites show smaller and broader SFS because $\Delta\nu_H$ is larger for these sites. In addition, as the laser frequency is moved away from the center of the inhomogeneous line, the amplitude of the SFS continuously decreases, as expected.

SFS provides a new window on inhomogeneously broadened lines with intrinsic detail and complexity. For example, recording of SFS spectra over a large fraction of the inhomogeneous profile may provide new information about the distribution of optical absorption energies available to the impurity centers. Furthermore, the scaling of the rms amplitude of the SFS spectra should reflect the number of centers in the probe volume, and the spectral content of the SFS signal can be used to estimate $\Delta\nu_H$. To demonstrate the former, we show in Figure 2 the rms amplitude of a large number of FM spectra versus N_H , the average number of centers in the probe volume per homogeneous linewidth, for a sequence of seven polycrystalline thin film samples. The samples were all prepared from a single concentration of pentacene in p-terphenyl, using different thicknesses. N_H was determined from the room-temperature optical density of the samples, the extinction coefficient, and the low-temperature

inhomogeneous broadening factor for these samples, $\Delta\nu_I/\Delta\nu_H = 1.3 \times 10^4$. The straight line is a least-squares fit to the data showing that the rms amplitude of the FM signals grows as $(N_H)^{0.54 \pm 0.05}$ which is consistent with the expected $(N_H)^{1/2}$ dependence. The vertical scatter in the points is also to be expected, because each FM spectrum was acquired over a different spectral range and therefore may be viewed as an independent statistical sample.

Estimates of $\Delta\nu_H$ can be extracted from the SFS spectra by a straightforward analysis. For scans like those in Figure 1 that span only a small part ($\Delta\nu = 800$ MHz) of the entire 2 cm^{-1} FWHM inhomogeneous line, one may reasonably assume that the distribution of energies available to the absorbing centers over this narrow range is independent of frequency. Then $\alpha(\nu)$ may be written

$$\alpha(\nu) = \sum_{i=1}^{N_0} \frac{c(\Delta\nu_H/2\pi)}{(\nu - x_i)^2 + (\Delta\nu_H/2)^2} \quad (2)$$

where x_i is a uniformly distributed random variable on $\Delta\nu$, and c is the integrated absorption strength per molecule. For the in-focus data in Fig. 1, $N_0 \approx 5 \times 10^7$. A useful way to study Eqn. 2 is to consider its autocorrelation, $\alpha \star \alpha$,

$$\alpha \star \alpha(\nu) = \int_{-\infty}^{+\infty} \alpha(\nu') \alpha(\nu' + \nu) d\nu'. \quad (3)$$

To get a lowest-order approximation to $\alpha \star \alpha$ for small ν , we note the cross terms in this integral yield small contributions unless the corresponding Lorentzian lineshapes have the same center frequency, so integration yields

$$\alpha \star \alpha(\nu) \approx N_0 c^2 \left(\frac{\Delta \nu_H / \pi}{\nu^2 + (\Delta \nu_H)^2} \right), \quad (4)$$

which is also a Lorentzian profile with FWHM equal to $2\Delta \nu_H$.

Equation 4 applies for the actual absorption, whereas the SFS spectra are related to $\alpha(\nu)$ by Eqn. 1. It would be ideal to apply an "inverse FM transform" to the FM data in order to study the actual shape of $\alpha(\nu)$. Such a transformation can be derived by Fourier techniques with the result

$$\alpha(\nu) \sim \mathcal{F}^{-1}[F(s)/2i \sin(2\pi \nu_m s)], \quad (5)$$

where \mathcal{F}^{-1} stands for the inverse Fourier transform and $F(s)$ is the Fourier transform of $F(\nu)$. Unfortunately, Eqn. 5 is difficult to compute for traces like those in Fig. 1 because of the lack of knowledge of the spectrum outside the range $\Delta \nu$ and the presence of multiple poles.

However, information can be derived about $\Delta \nu_H$ by considering the autocorrelation of the FM signals, $F \star F(\nu)$. In the limit $\nu_m > \Delta \nu_H$, the leading dependence of $F \star F$ for small ν is the same as that for $\alpha \star \alpha$ within a constant factor. Thus an estimate for $\Delta \nu_H$ can be derived from the curvature of $F \star F$ at $\nu = 0$, i.e.,

$$\Delta \nu_H \approx -2F \star F(0)/F \star F''(0), \quad (6)$$

where the double prime signifies second derivative. It is clear that by computing higher-order corrections to the expected form of $F \star F$, more accurate formulae for the estimation of $\Delta \nu_H$ may be derived.

We have used computer simulations of Eqns. 1 and 2 with $N_0 = 10^6$ to test the accuracy of Eqn. 6 in estimating $\Delta\nu_H$ and find that Eqn. 6 overestimates the actual value by 15-20 % on average. This supports the validity of the estimation of $\Delta\nu_H$ using autocorrelations of FM spectra. For our samples, we find $\Delta\nu_H \approx 9.6$ MHz for the O_1 site at 1.4 K by averaging the results from 11 spectra. This value was observed to be independent of N_H and is consistent with the value of $\Delta\nu_H$ we deduce from our measured hole widths. However, it is somewhat larger than the previously reported^{13, 14} values for unknown reasons. Power broadening is not greatly affecting our data even though the intensity of the carrier is greater than the saturation intensity of $\approx 10\text{mW/cm}^2$. This is because the intensity of each sideband is only 6.7×10^{-3} of the carrier and the decay time for any saturation produced by the carrier⁸ is shorter than the time between the arrival of the carrier and a sideband at a given spectral location.

SFS should be a general feature of all inhomogeneously broadened lines in solids, and even in gases if measurements are performed on a time scale shorter than the collision time. We expect that SFS should be observable for color-center absorptions and possibly for impurity vibrational mode transitions in crystals as well as in amorphous media. We note that SFS imposes a fundamental limit on the detectability of shallow spectral features in inhomogeneous lines.

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REFERENCES

1. A. M. Portis, Phys. Rev. 91, 1071 (1953).
2. A. M. Stoneham, Rev. Mod. Phys. 41, 82 (1969).
3. A. L. Schawlow, in *Advances in Quantum Electronics*, proceedings of the Second International Conference on Quantum Electronics, edited by J. R. Singer, (Columbia Univ., New York, 1961), pp. 50-64.
4. L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part 1*, (Pergamon, Oxford, 1980), p. 9.
5. For a description of background problems for liquid hosts, see D. C. Nguyen, R. A. Keller, and M. Trkula, J. Opt. Soc. Am. B 4, 138 (1987).
6. G. C. Bjorklund, Opt. Lett. 5, 15 (1980).
7. R. W. Olson and M. D. Fayer, J. Phys. Chem. 84, 2001 (1980).
8. H. de Vries and D. A. Wiersma, J. Chem. Phys. 70, 5807 (1979).
9. G. C. Bjorklund, M. D. Levenson, W. Lenth, and C. Ortiz, Appl. Phys. B 32, 145 (1983).
10. T. P. Carter, M. Manavi, and W. E. Moerner, to be published.
11. W. E. Moerner and M. D. Levenson, J. Opt. Soc. Am. B 2, 915 (1985).
12. W. E. Moerner, A. J. Sievers, R. H. Silsbee, A. R. Chraplyvy, and D. K. Lambert, Phys. Rev. Lett. 49, 398 (1982).
13. F. G. Patterson, W. L. Wilson, H. W. H. Lee, and M. D. Fayer, Chem. Phys. Lett. 110, 7 (1984).
14. F. G. Patterson, H. W. H. Lee, W. L. Wilson, and M. D. Fayer, Chem. Phys. 84, 51 (1984).

FIGURE CAPTIONS

Figure 1. FM spectra in the quadrature phase for a single crystal of pentacene in p-terphenyl. (a) No light on the detector. (b) $3 \mu\text{W}$ on the detector at a wavelength not in resonance with the O_1 site absorption. (c),(d) FM spectra at 1.4 K near the peak of the O_1 absorption at 592.3 nm with a focused spot. (e) A new spot on the sample, same spectral range as (c). (f) Laser center frequency offset by 50 MHz from that for (e). (g) Large laser spot (0.75 mm diameter). (h) Persistent hole burned in the spectral range of trace (g). (i) 1.4 K, focused spot. (j) 5.6 K, same location. (k) 7 K. The vertical scale is exact for (c) and (d); all the other traces have the same scale but are offset vertically for clarity. One volt corresponds to a change in αL of 1.1×10^{-3} . The detection bandwidth was 0.1 Hz to 300 Hz and $\nu_m = 58.1$ MHz with $M = 0.16$. The frequency scale was calibrated by optically observing the sideband spacing.

Figure 2. RMS amplitude of FM signal versus N_H , using in-focus spectra similar to trace 1(c) with $\nu_m = 50$ MHz. The solid line is a least-squares fit.

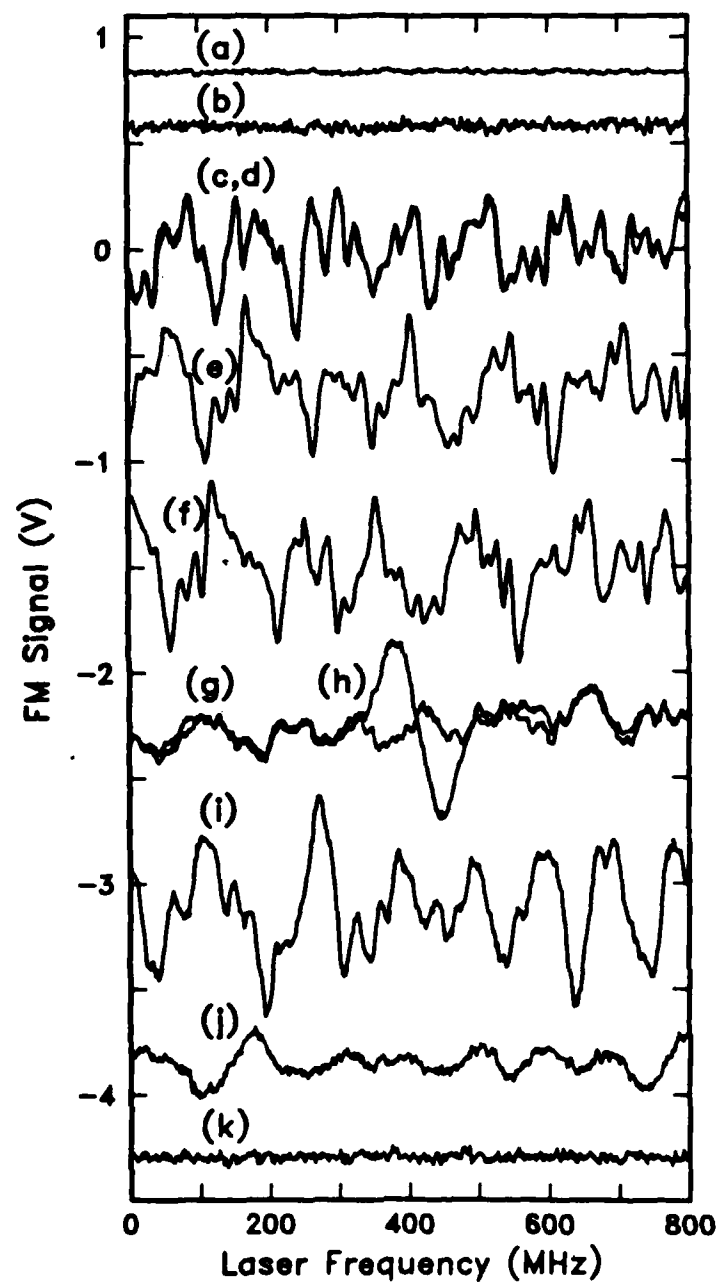


Fig. 1

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